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Oxidation Catalyst Effect on CNG Transit Bus Emissions

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ABSTRACT

Recently, the California Air Resources Board (CARB) has reported that tailpipe emission samples from a compressed natural gas (CNG)-fueled transit bus without aftertreatment had measurable levels of toxic compounds such as formaldehyde (HCHO) and nanoparticle (= 50 nm) and mutagen emissions (Ames assay) that in some cases were greater than that of a similar diesel transit bus equipped with either a diesel oxidation catalyst (DOC) or a diesel particulate filter (DPF) and fueled by ultra-low sulfur diesel (ULSD) [1, 2, 3]. Therefore, CARB has investigated the effectiveness of oxidation catalyst (OC) control for CNG bus applications. This study includes results for regulated gaseous and non-methane hydrocarbon (NMHC) emissions, non-regulated hydrocarbon emissions of toxic risk significance, and total particulate matter (PM). Two driving cycles were investigated: the Central Business District (CBD) cycle and Steady-State (SS) cruise condition at 55 mph.

The catalyst showed statistically significant reduction of total PM, total hydrocarbons (HC), NMHC, and carbon monoxide (CO). HCHO emissions were reduced by the catalyst by over 95% over both CBD and SS cycles. 1,3-butadiene emissions were reduced to levels below detection. Toxic aromatic HC's such as benzene also appeared to be reduced by the catalyst, but a larger data set is required to establish statistical significance. Little effect of the catalyst was found on methane (CH_4) and oxides of nitrogen (NO_X).

INTRODUCTION

Recognizing the harmful effects of diesel exhaust PM, CARB developed a number of strategies and control measures to reduced the risk of exposure to diesel exhaust PM that are to be phased in over the next several years [4]. Other regulatory agencies are working towards reducing diesel exhaust PM exposure risk as well. In this regard, the use of CNG to fuel heavy-duty transit buses is currently considered a "green" alternative to conventional diesel buses. In the South Coast Air Basin of California (SCAQMD), CNG-fueled buses are required for some new fleet acquisitions [5]. In general, the regulatory measures that promote the use of CNG technology are meant to curtail toxic diesel exhaust PM emissions from new and existing on-road and off-road sources. Although it has been shown that CNG-fueled buses, with or without aftertreatment, offer significant reductions in PM and NO_X over conventional diesel-fueled vehicles, additional information was needed on the non-regulated species, both known toxins or others, found in their emissions profile. For this reason, CARB has embarked on a comprehensive effort to study tailpipe emissions from in-use, late-model CNG and diesel transit buses. In this paper, we provide an update of results for two CNG buses equipped with OC control. One of these buses was tested with and without its OC.

Findings from the initial phase of CARB's study of transit buses showed that a late-model CNG transit bus without aftertreatment had measurable levels of toxic compounds [1]. For example, over the CBD, the uncontrolled CNG bus emitted nearly one gram per mile of HCHO. Similar levels were observed from CNG buses studied by Gibbs [6]. For comparison, an older model medium duty vehicle (i.e., 1893 Ford F-250 pick-up powered by a V8 Navistar engine without catalyst) has average HCHO emissions of approximately 120 mg/mi over the Federal Test Procedure cycle [7]. In an effort to quantify a control strategy for HCHO and other known toxic air contaminants (TAC) also identified in the emissions profile for an uncontrolled CNG bus, the effectiveness of OC control was investigated. Currently, OC's for CNG buses exist as off-the-shelf items. However, they are typically not used due to the inherently low emission levels for regulated pollutants from CNG engines; hence, their ability to meet urban bus emission standards without aftertreatment. Others have studied the emissions from diesel and CNG engines [8]. The use of OC on CNG applications has been reported to yield significant reductions in SOF, in general, and CO, HC, NMHC, and PM, specifically. It is recognized that an OC offers HCHO control from CNG engines. However, the specific reduction of other toxic compounds such as 1,3-butadiene and benzene have not been reported. Furthermore, the effect of an OC on other chemical species such as polycyclic aromatic hydrocarbons (PAH) or on the number of ultrafine (< 100 nm) particles is not known. Johnson reported that the use of OC for diesel applications has not led to a reduction in the number of particles emitted [9]. The impetus of the present study was to measure the emissions of various substances of toxic significance and to determine to what extent an OC benefits the emissions exhaust profile for a CNG engine.

EXPERIMENTS AND PROCEDURES

In this study, CARB used an identical approach to that reported previously [10]. Briefly, bus emissions were determined using the procedures outlined in the Code of Federal Regulations (CFR) [11]. Testing was conducted at CARB's Heavy-duty Emissions Testing Laboratory (HDETL) located in Los Angeles. The HDETL is equipped with heavy-duty engine and chassis dynamometers, which are served by a Horiba critical-flow venturi constant volume sampling (CVS) dilution tunnel. For this program, the CVS was operated, again, at approximately 2500 scfm. A conventional bench of gas analyzer was used to determine regulated emissions. Gas analyzer zero and span readings were checked routinely in accordance with the CFR. National Institute of Standards and Technology (NIST)-traceable protocol gases were used for calibrations. A secondary dilution tunnel with high-efficiency particulate air (HEPA)-filtered air was used to collect PM emissions.

Fuel and lubricating oil samples were collected and analyzed by commercial laboratories. All of the CNG fuel necessary for testing was obtained from one of the refueling stations that serve the Los Angeles County Metropolitan Transit Authority (LACMTA). Fuel samples were taken directly from the buses and collected in stainless steel canisters under pressure. Oil samples were collected from the vehicles before and after emissions testing. In general, the low-ash oils exhibited normal levels of additives and wear metals. All CNG samples were found to be in compliance with CARB's specifications.

Vehicles and Cycles

Two buses were tested in three vehicle configurations. These were, 1) a CNG 40-passenger New Flyer bus powered by a 2000 Detroit Diesel (DDC) Series 50G engine without aftertreatment, 2) the same DDC CNG bus, but equipped with an original equipment manufacturer (OEM) OC, and 3) a CNG 40-passenger New Flyer bus powered by a 2001 Cummins Westport (CWstprt) C Gas Plus engine and OEM-equipped with an OC. For this bus, with an odometer reading of 18,700 miles, the OC was not removed for baseline testing. Both buses were powered by heavy-duty, lean burn, closed loop controlled, dedicated CNG engines. The DDC engine is a diesel derivative. The DDC CNG bus was previously tested twice by CARB staff in the initial phase of their study [10]. This time, the vehicle odometer read approximately 56,600 miles. For this phase, a new OC was installed on this bus by the engine manufacturer. This bus was put into revenue service for approximately one month to "de-green" the catalyst. The accumulated mileage on the OC was approximately 4,300 miles. Conservatively, assuming a nominal speed of 20 mph, the top speed of the CBD cycle, the OC was aged for at least 215 hours. This conditioning time was more than double the number of hours reported by other investigators [12]. The OC-equipped DDC CNG bus is an optional ultra-low-emission package offered to transit agencies. The buses were tested with a simulated passenger load of approximately 50%.

One transient duty cycle, the CBD, and one SS "cycle" were included in this study. These cycles were two of the five previously used in the CARB study [10]. The testing protocol included duplicate sequences for each emission sample. A test sequence was composed of four individual CBD or CBD-equivalent SS cycles run back-to-back. The first cycle was for vehicle conditioning and warm-up. PM sample collection was conducted over the subsequent three cycles. Thus, PM samples were collected during approximately 30 minutes of bus operation on the dynamometer. Tunnel background (TB) samples were collected identically, with the bus exhaust disconnected from the CVS.

Chronologically, the DDC CNG bus was retrofitted with its OC by the OEM and sent into revenue service. Emissions testing began with the CWstprt bus, followed by the OC-equipped DDC bus. The OC was then removed from the DDC CNG bus by the OEM for baseline testing.

Sample Collection and Analysis

Similar to previous work, regulated and un-regulated emissions were determined for all three vehicle configurations [10]. Again, all regulated gaseous and PM emissions were collected and analyzed in adherence with the procedures for heavy-duty vehicle testing specified in the CFR [11]. Samples were collected in duplicate over two test sequences, each sequence consisting of six individual CBD or CBD-equivalent SS cycles. Gas samples using a heated line were collected to determine total HC emissions using a conventional flame ionization detector (FID) analyzer. CH_4 content was determined using gas chromatography (GC). A FID response factor for CH_4 was also determined. Total NO_X emissions, assumed to be the sum of nitrogen oxide (NO) and nitrogen dioxide (NO_2), were determined with a pair of chemiluminescence (CLM) analyzers via time alignment of the modal signals against the bus speed trace as previously reported [8]. The time alignment compensated for response delays. NO_2 was calculated as the difference between NO_X and NO. CO and CO_2 emissions were determined from Tedlar bag samples. Gas emission results were corrected for sampling conditions. PM samples were collected on standard 70 mm Teflon-coated filters (Model T60A20 with a 98% efficiency at ≥ 0.1 µm) at a filter face temperature of approximately 51^{o}C or less. Filters were conditioned before and after at 50% relative humidity and 25^{o}C and analyzed gravimetrically using a microbalance as per CFR requirements.

Speciation of volatile organic compounds (VOC) by GC was conducted from samples collected in 8L baked Tedlar bags. An average NMHC density of 16.33 g/scf was used. Sample collection and analysis followed the NMOG procedure used by CARB for speciation of gasoline exhaust as previously reported [10,13]. Briefly, after the CO/CO_2 Tedlar bag sample was collected, a pump was used to transfer a sample to the small 8L bag. A background sample from the background bag was also taken. VOC concentrations were determined using a flame ionization detector following cryogenic pre-concentration. Small bag samples for speciation were collected in duplicate each over a single cycle, the third cycle in a test sequence.

Diluted exhaust samples for identification of carbonyl compounds were collected via a heated line from the CVS and drawn through Sep-Pak cartridges coated with 2,4-DNPH. Carbonyl compounds react with DNPH and form hydrazones. These were solvent extracted and analyzed by high-precision liquid chromatography (HPLC) within a few hours of collection. Cartridge samples were collected over a single cycle, the third cycle in a test sequence, in duplicate for all three vehicle configurations. Thirteen carbonyl compounds were analyzed as listed in Appendices B.

Additional samples were collected for: 1) elemental and organic carbon analyses, 2) extractions for Ames bioassay analysis in tester strains TA98 and TA100 with and without the incorporation of microsomal enzymes S9, and 3) PAH analyses of PM-bound, volatile, and semi-volatile compounds [14]. Finally, two Scanning Mobility Particle Sizers (SMPS) were used for particle size distribution and particle number concentration measurements. Results will be reported in future publications.

RESULTS AND DISCUSSION

In this paper, we report results for regulated and toxic VOC emissions. The effect of OC on the particle size distributions for the CNG buses have been described preliminarily by Holmén and Ayala (2003) [15]. Mean results and standard deviations are tabulated in Appendix A and B. Net emissions are not reported in this study. Instead, tunnel background "emissions" are consistently reported along with results.

Regulated Emissions

The regulated emissions results presented in this paper reflect emissions averaged over two test sequences with each test sequence result being an average of three cycles. Recall that each test sequence was composed of four cycles run back-to-back.

a)

b)

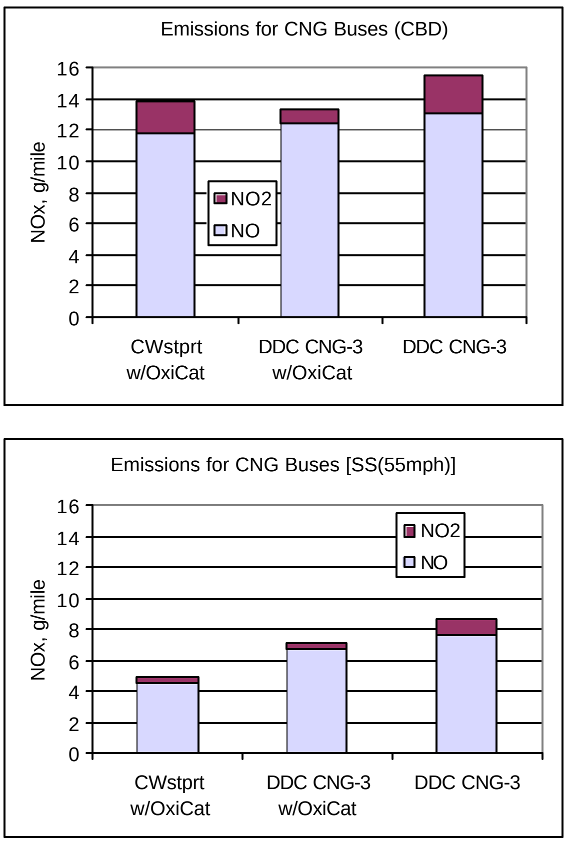


Figure 1. Average CNG bus NO_X results. (Throughout this paper, CNG-3 on label for DDC bus refers to third and most recent tests). Data and statistics in Appendix A.

Figure 1 illustrates NO_X emissions results. Over the CBD, average NO_x emissions of 15.55 g/mi were determined for the DDC CNG bus when tested without OC. The same bus equipped with OC resulted in NO_X emissions of 13.3 g/mi. The catalyst on this bus was not expected to affect its NO_X emissions. The differences illustrated in Figure 1 for both cycles are within measurement uncertainty and may also be attributed to run-to-run variability. The CWstprt bus resulted in average NO_X emissions of 13.9 g/mi over the CBD cycle. The NO_X emissions were dominated by NO, with NO_2 fractions falling below 20% of the total NO_X results. Specifically, the DDC bus with and without OC over the CBD yielded average NO_2 emissions of 1.0 g/mi and 3.3 g/mi, respectively. The CWstprt bus NO_2 emissions were 2.1 g/mi.

NO_X gram/mile emissions over SS were lower than CBD emissions. In this case, average NO_X emissions for the DDC bus with and without OC were 7.1 g/mi and 8.7 g/mi, respectively. The CWstprt bus had NO_X emissions of 4.9 g/mi. Similar to CBD results, NO_X emissions over the SS were dominated by NO. The NO_2 emissions over SS for the DDC with and without OC were 0.4 g/mi and 1.1 g/mi, respectively. The CWstprt bus had average NO_2 emissions 0.4 g/mi over the SS cruise.

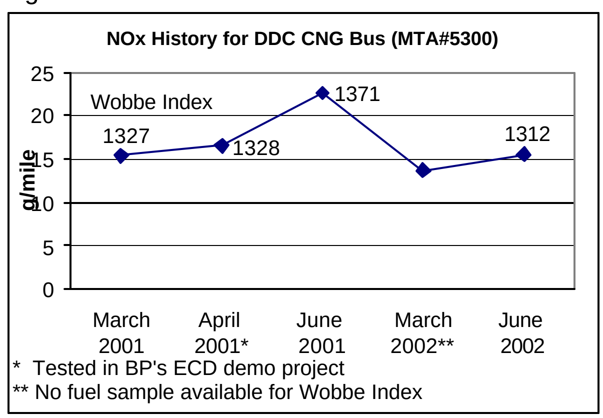


Figure 2. Average NO_X results for DDC CNG bus. (April 2001 results were obtained by West Virginia University for the same bus tested under the BP/ARCO ECD demonstration project in Southern California).

The variability of NO_X emissions from natural gas vehicles has been observed by others and vehicle state of maintenance may play a role [16]. In addition, Graboski et al. (1997) reported that some of this variability may be attributed to variations in the composition of natural gas, which can produce changes in stoichiometry and octane number [12]. In this research program, the same DDC CNG bus has been tested over a period of approximately two years and average NO_X emission levels have been found to fluctuate between approximately 14 g/mi and 23 g/mi as illustrated in Figure 2. Both vehicle maintenance and fuel quality are possible suspects for this variation in NO_X emissions.

For all tests, the bus has been fueled with refueling station gas, whose composition has varied in time as reported by Ayala and co-workers (2002) [10]. For tests conducted in June 2001, which showed a marked increase in NO_X emissions, as illustrated in Figure 2, the CNG fuel contained a lower than expected methane content and a higher content of higher hydrocarbons, primarily ethane and propane. The fuel composition did not meet the current California CNG motor vehicle fuel specifications illustrated in Appendix C. We suspect fuel blending as the reason. Methane content was lower than the required minimum by approximately one percent. Additionally, C3+ (all hydrocarbon species heavier than and including propane) and ethane contents exceeded the maximum specifications by approximately one percent and a half percent, respectively.

The increased higher hydrocarbons content of this gas resulted in an increase in the heating value and Wobbe Index. Wobbe Index is a measure of the fuel interchangeability with respect to its energy content and metered air/fuel ratio. It can be calculated from the energy content and relative density of the gas, *Wobbe Index = Higher Heating Value / sqrt(Relative Density)*. Wobbe Indices for the different fuels tested are noted in Figure 2.

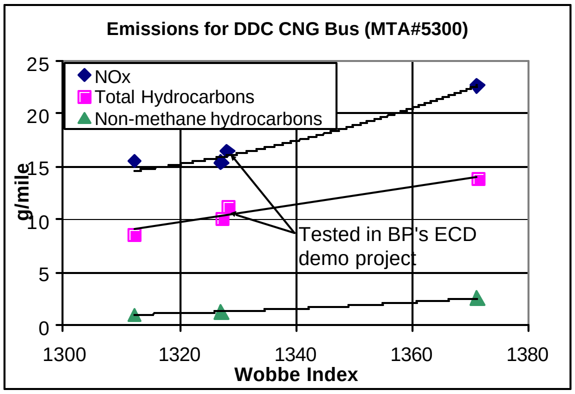


Figure 3. Average NO_X, Total Hydrocarbon, and Non-methane hydrocarbon results for DDC CNG bus.

The measured NO_X emissions for the DDC CNG bus are shown plotted as a function of Wobbe Index in Figure 3. Measured total hydrocarbons and non-methane hydrocarbons are also plotted as a function of Wobbe Index in this figure. NO_X emissions appear to increase with Wobbe Index. However, the simultaneous increase in both total hydrocarbon emissions and NO_X emissions appears anomalous for a fuel related response. The total hydrocarbon emissions increase, indicating reduced combustion efficiency, is inconsistent with the NO_X emissions increase associated with higher combustion temperature.

The observed NO_X emissions increase with increased Wobbe Index for the DDC CNG bus is significantly higher than that observed for other heavy-duty closed loop engine data [17]. Closed loop heavy-duty engines are more tolerant to wide variations in fuel quality. The NO_X increase seen with the DDC CNG bus is more consistent with that observed for a heavy-duty open loop engine [17]. The observed anomalous relationship between the increase in NO_X emissions and total hydrocarbon emissions for the DDC bus leaves doubt as to whether it can be attributed to the fuel quality. Ultimately, this observed variability may be attributed to vehicle, fuel, or variations in both.

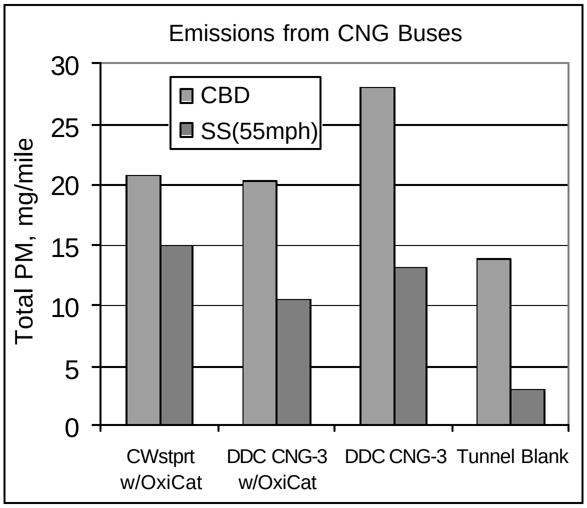
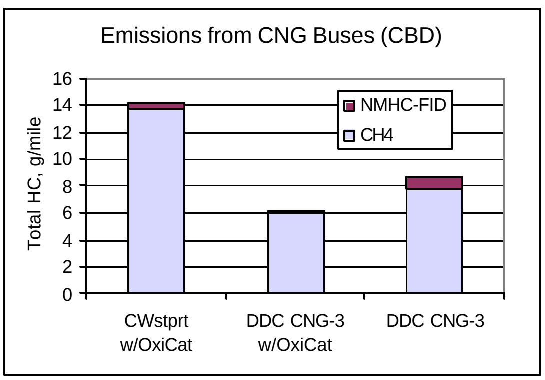


Figure 4. Average CNG bus Total PM Emissions. Data and statistics in Appendix A.

The effect of the OC on the DDC CNG bus total PM emissions is evident in Figure 4, which shows average results that have not been corrected for the tunnel background levels also illustrated. In general, the transient duty cycle produced higher g/mi PM emissions than the SS condition for all three bus configurations. The OC reduced PM emissions over the CBD cycle by approximately 28%, from an average of 28 mg/mi to 20 mg/mi. The CWstprt bus, which is OEM equipped with an OC, had statistically the same PM emissions to the DDC bus over the CBD. Over the SS run, the OC on the DDC bus produced a statistically significant reduction of approximately 17% from a level of 13 mg/mi down to 11 gm/mi. In contrast, the CWstprt bus resulted in emissions of 15 mg/mi over the SS.

The tunnel background "emissions" illustrated in Figure 4 are results averaged over the test sequences for all three bus configurations and normalized by the equivalent cycle miles. In the case of the CBD - TB results, the "emissions" collected for each vehicle configuration over a ~30 min test sequence (three CBD cycles back to back, each of approximately 10 min in duration) were divided by 6 miles, or the approximate distance traveled in three CBD cycles. In this case, the TB was equivalent to approximately 14 mg/mi or slightly over half of the emission factors determined for the three bus configurations. Over the SS, the TB level was lower or approximately 3.0 mg/mi. It is noted that these TB levels are not excessive, but rather typical of those found in heavy-duty emissions laboratories [18].

a)



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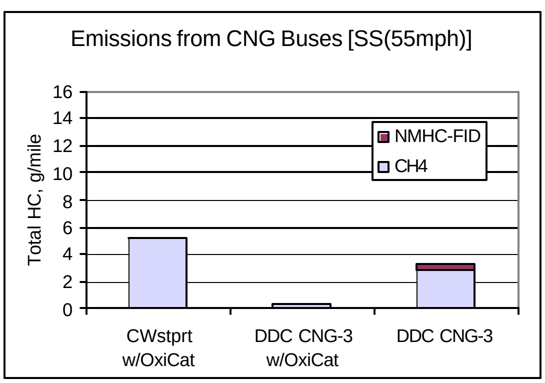

Figure 5. Average CNG bus total HC Emissions. Data and statistics in Appendix A.

In the case of the average total HC emissions illustrated in Figure 5, the OC on the DDC CNG bus yielded a reduction of approximately 29% over the CBD cycle. That is, total HC average emissions of 8.7 g/mi were reduced by the OC to 6.2 g/mi. The CWstprt bus resulted in total HC average emissions of 14.1 g/mi over the CBD cycle. As expected, CH_4 accounted for the majority of the total HC emissions measured for both the DDC and CWstprt buses. The NMHC fractions in Figure 5 are shown for completeness. They were determined following the CFR NMHC procedure based on the use of a FID analyzer. Later in the paper, estimates of NMHC emissions based on GC hydrocarbon speciation of Tedlar bag exhaust samples are presented. It is noted that the OC's on both CNG vehicles are not aftertreatment devices designed to control CH_4, but rather HCHO emissions, as will be shown later.

Over SS, the CWstprt bus, at 5.3 g/mi, resulted again in higher total HC emissions than the DDC bus. Without OC, the DDC bus emitted 3.3 g/mi total HC. The OC reduced these emissions by 86% to 0.5 g/mi. Again, CH_4 dominated the total HC measured over the SS test condition.

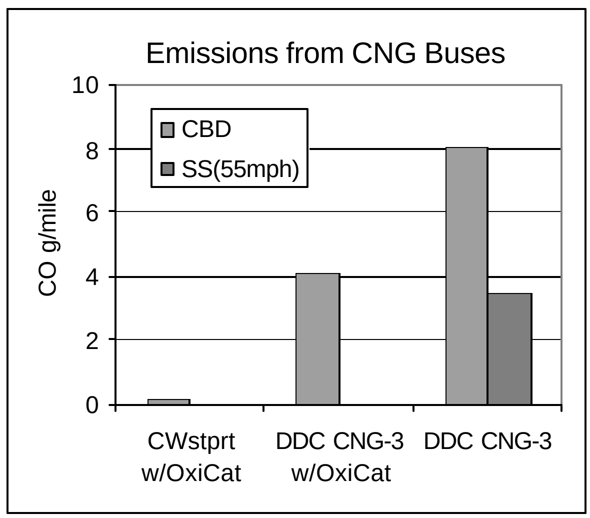

Figure 6. Average CNG bus CO Emissions. Data and statistics in Appendix A.

The emission benefits offered by the catalyst for CNG bus applications were also evident in the CO results shown in Figure 6. The catalyst in the DDC bus was found to yield significant reductions over both the CBD and SS cycles. Over the CBD, 49% reduction in CO emissions from 8.0 g/mi to 4.1 g/mi were determined. The reduction of CO emissions by the OC was more dramatic over the SS cycle. Average emissions of 3.5 g/mi were reduced to 0.01 g/mi or near detection limits. Equally effective, the OC on the CWstprt resulted in high conversion of CO emissions, resulting in average emissions of 0.2 g/mi and 0.02 g/mi over the CBD and SS cycles, respectively.

Un-regulated Emissions

The mass emissions of the non-regulated VOC species analyzed in this study for the two driving cycles tested are summarized in Table A of Appendix B. These figures represent averages of replicate tests ± one standard deviation. Tunnel blank run results are shown in Table B of Appendix B. Only one tunnel blank was analyzed per vehicle configuration, however each analysis is given two values corresponding to equivalent emissions from either a SS or a CBD cycle. In other words, the tunnel 'emission' was measured as a total mass per test which has a separate mg/mile of driving cycle equivalent. For driving cycle equivalents, the tunnel mass emission is divided by the distance traveled by the vehicle during the cycle (2.0 and 8.7 miles for SS and CBD, respectively).

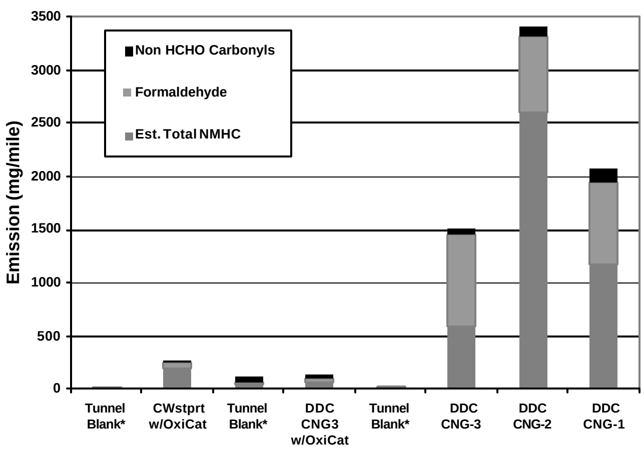

Figure 7. Estimated total NMOG emission for the CBD driving cycle. Estimated NMOG = sum of 13 carbonyl species and estimated total gas phase NMHC by GC. * = Tunnel blanks correspond to adjacent vehicle configuration (see text).

From the speciated hydrocarbon emission values by GC and HPLC (carbonyls), an estimated total non-methane organic gas (NMOG) emission can be calculated. Figure 7 shows the average NMOG emission values for the CBD driving cycle for the three vehicle configurations of the present phase of this study and their corresponding tunnel blanks. Because the DDC bus was also tested in the former phase of this study, the emission values from those two vehicle configurations (DDC CNG-1 and 2), reported by Kado et al. are included for comparison [3]. It is clear from figure 7 that NMOG emissions are significantly reduced by the use of an OC.

Figure 7 shows the average results for NMHC and carbonyl emissions for the DDC and CWstprt buses over the CBD cycle. NMHC emissions were determined from GC analysis. Analysis for 13 carbonyls species listed in Figure 11 were conducted. Results were not corrected for TB levels, also shown in the figures. For the DDC bus, CNG–1 and CNG–2 correspond to earlier results from testing conduced in 2001 and to be reported elsewhere by Kado and co-workers [3]. They are included for comparison. CNG-3 corresponds to the new results from the present study conducted in 2002. The variability over time of total NMHC and carbonyl emissions is evident for the DDC bus.

Present CBD results (see DDC CNG-3) for the DDC bus show that average NMHC emissions of 588 mg/mi were reduced 89% by the OC to 66 mg/mi. The single largest emission reduction by the OC occurred for ethene, where an average uncontrolled emission of 342 mg/mi was reduced to 3.3 mg/mi. Similarly, the total carbonyl emissions of 929 mg/mi from the DDC bus were reduced 92% by the OC to 77.6 mg/mi. While the CWstprt bus had total NMOG average emissions of 264 mg/mi over the CBD and slightly higher than the OC-equipped DDC bus, approximately 2/3 of those emissions or 184 mg/mi were NMHC with the remaining 1/3 or 80 mg/mi being carbonyl emissions.

For the uncontrolled CNG bus, HCHO accounts for the largest fraction of the nearly 1 g/mi carbonyl emissions over the CBD cycle as illustrated in Figure 8. Specifically, HCHO has ranged from approximately 86% to 92% of all carbonyl emissions measured over time. Presently, average HCHO emissions were 860 ± 60 mg/mi. These results are in good agreement with those of Gibbs (1999) [6]. The OC was 96% effective in the reduction of HCHO emissions from the DDC bus. For both the OC-equipped DDC and CWstprt buses over the CBD cycle, HCHO emissions were 38.4 mg/mi and 56.8 mg/mi, respectively. Equivalent TB levels ranged from 13 to 20 mg/mi during testing of these three vehicle configurations.

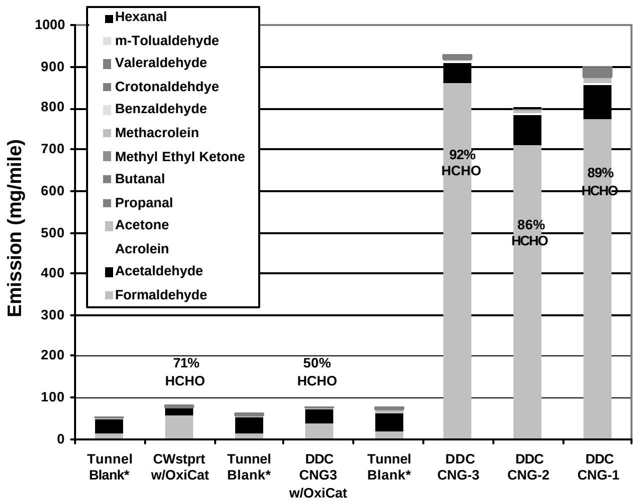

Figure 8A. Average carbonyl emissions by species for the CBD driving cycle. * = Tunnel blanks correspond to adjacent vehicle configuration (see text).

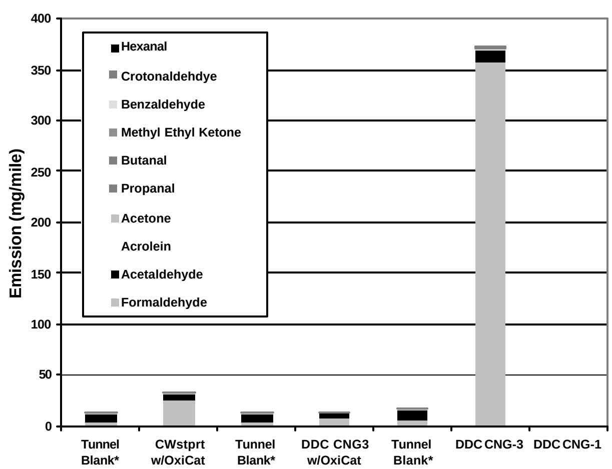

Figure 8B. Average carbonyl emissions by species for the SS driving cycle. * = Tunnel blanks correspond to adjacent vehicle configuration (see text).

The second largest contributor to carbonyl emissions was acetaldehyde. Some reductions in acetaldehyde levels offered by the OC were also observed. Specifically, the DDC bus acetaldehyde emissions of 50.7 mg/mi were reduced by the OC to 32.6 mg/mi. The CWstprt bus yielded lower acetaldehyde emissions of 19.4 mg/mi. However, the equivalent acetaldehyde TB levels for the CBD results ranged from 32 to 44 mg/mi as illustrated in Figure 8.

Similar trends were observed over the SS tests. In this case, the variability in results from the DDC CNG bus over time is apparent again. Carbonyl emissions for the DDC bus over the SS were less than half of those measured over the CBD cycle. Again, dramatic reductions with the OC on the order of 96% were determined for HCHO emissions. Over SS tests, both DDC and CWstprt OC-equipped buses yielded total average carbonyl emissions of 13.3 mg/mi and 32.5 mg/mi, respectively. In contrast, without the OC, the DDC bus had SS carbonyl emissions of 373 mg/mi.

Figure 9 shows the sums of the average emissions of benzene, toluene, ethylbenzene, and xylenes (BTEX) for the 3 vehicle configurations of the present study compared to the two CNG configurations studied previously. Although the individual measurements for benzene and toluene were reasonably reproducible (Appendix B, Table A), the three tunnel blank measurements for this study showed significant variability in total BTEX as seen in Figure 9. Generally BTEX emissions ranged from 1.5 to 4 mg/mile for CBD cycles and were much lower for SS cycles as expected. There seems to be marked reduction for the DDC CNG-3 bus from the addition of the OC for the SS cycle, but overall it is difficult to determine a quantitative effect of the OC from our data set.

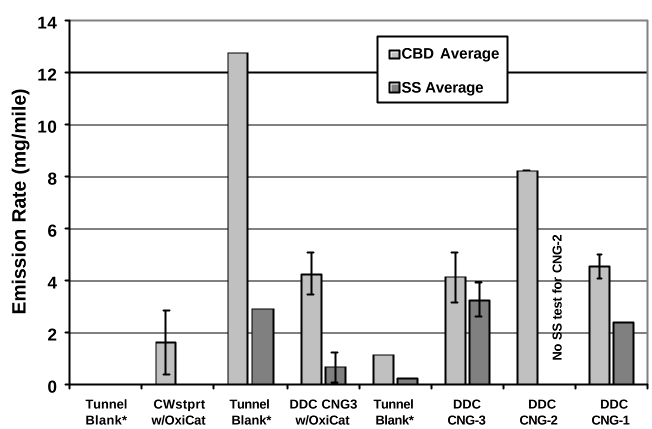

Figure 9. Average total BTEX emissions by driving cycle. * = Tunnel blanks correspond to adjacent vehicle configuration (see text).

Benzene dominated the BTEX emissions (Appendix B, Table A) and the emission factors are displayed in Figure 10. These data provide more convincing evidence for a reduction due to the use of an OC. An average of the three values from the DDC bus without OC tested in the current and previous phase of the study is greater than 3 mg/mile while the emission rate is only 0.60 for the DDC CNG-3 w/OxiCat bus.

The results of light end GC analysis of NMHC emissions of C_6 and fewer non-carbonyl hydrocarbons show that the predominant species are ethane and ethene (Appendix B, Table A). There are smaller contributions from acetylene, propane, and propene, with lower values from methylpropane and butane. This is consistent with a CNG-diesel comparative study by Clark et al. (1995) who found that ethane, ethene, and propane were the most abundant CNG NMHC emissions [16]. A comparison of the emission of these species with and without OC reveal dramatic reduction by the OC as expected. Acetylene emission is completely reduced while ethene, propene and larger hydrocarbons are reduced by one or more orders of magnitude. Significant reduction of propane and ethane are also observed.

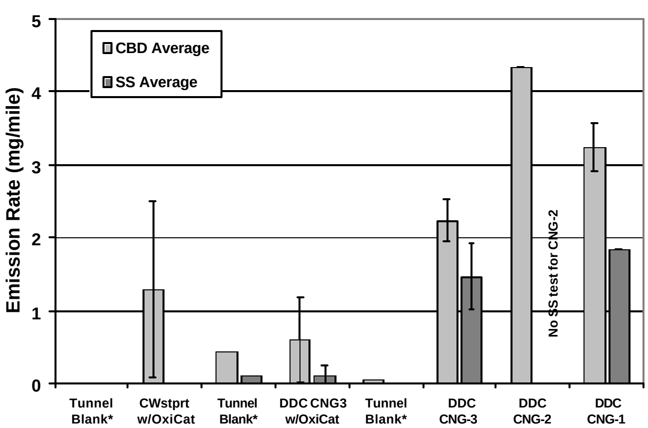

Figure 10. Average benzene emissions by driving cycle. * = Tunnel blanks correspond to adjacent vehicle configuration (see text).

One final analyte of interest was 1,3-butadiene and average emissions results are summarized in Figure 11. Originally, the DDC bus was determined to emit 1,3-butadiene at nearly 3.5 g/mi (see DDC CNG-1 in Figure 11) over the CBD. Subsequent testing of the same vehicle revealed butadiene emissions at lower levels. At present, baseline 1,3-butadiene emissions were determined at 0.39 mg/mi and 0.1 mg/mi over the CBD and SS, respectively. The application of OC resulted in 1,3-butadiene levels below detection for both CBD and SS cycles. Similarly, results for the OC-equipped CWstprt bus revealed that its 1,3-butadiene emissions were below detection. No 1,3-butadiene was detected in any tunnel blank measurement. As illustrated by Figure 11, high variability in 1,3-butadiene emissions for the DDC bus without OC were observed over time. In this study, Tedlar bag samples were analyzed for VOC composition immediately after collection in order to minimize the decay known to occur in vehicle exhaust. Further research is needed to determine the cause of the variability of the 1,3-butadiene emissions.

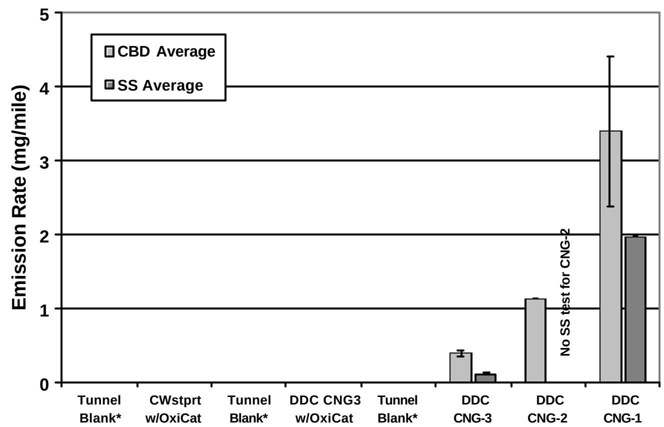

Figure 11. Average 1,3-butadiene emissions by driving cycle. * = All tunnel blanks were below detection limits.

CONCLUSIONS

This paper offers a summary of the effect of oxidation catalyst control for CNG transit bus applications over two duty cycles, the CBD cycle and SS operation. The results discussed represent a snapshot of two buses, not a true fleet average. Consistently, the transient cycle produced higher emissions when expressed in units of mass emitted per unit distance traveled by the vehicle. In general, the OC installed by the OEM on the DDC CNG bus for this study revealed significant and consistent reductions in some regulated and un-regulated emissions. Specifically, the OC showed statistically significant reductions of total PM, total HC, NMHC, and CO over both CBD and SS cycles. In contrast, the OC had little effect on NO_X and CH_4. NO_X emissions in the form of NO_2 for CNG buses, with or without after-treatment, were well below 20%. Large fluctuations in NO_X emissions over time have been observed for the DDC CNG transit bus. The reason for this variability is not known. CH_4 accounted for greater than 87% of the total HC emissions for both buses.

In accord with observations made by others, HCHO was confirmed to be the most prevalent compound in the carbonyl emissions. However, the effect of the OC on some carbonyl emissions, especially HCHO, was remarkable. HCHO emissions were reduced by the OC by 95+% over the two cycles investigated. Reductions produced by the OC also included acetaldehyde, however, tunnel carryover did not permit an accurate determination of the level of reduction. Benzene and toluene accounted for a significant portion of total BTEX emissions from an uncontrolled CNG bus. In this case, the OC appears to be effective at reducing benzene emissions, specifically, and total BTEX emissions in general. 1,3-butadiene emissions, which had only been observed in CNG bus exhaust, not in diesel bus samples, were reduced to levels below detection limits by the OC [3]. In general, these reductions were confirmed by the results for the OC-equipped CWstprt bus. However, the uncertainty in Benzene emissions was, in one case, ± 97%. Finally, total PM and some HC levels in TB measurements suggest and support the need for improved sampling protocols for the evaluation of “clean” engine technology.

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APPENDIX A

Mean Emissions and Tunnel Blank Results and Standard Deviations.

Bus Type	TEST CYCLE	PM g/mile	THC g/mile	CO g/mile	NOX g/mile	CO2 g/mile	CH4 g/mile	NO2 g/mile
Cummins Westport	SS@55(30min)	0.0162	5.36	0.02	4.73	976.92	5.23	0.40
	SS@55(30min)	0.0138	5.27	0.02	5.12	975.07	5.15	0.46
	Mean	**0.0150**	**5.31**	**0.02**	**4.93**	**976.00**	**5.19**	**0.43**
	Stand. Dev.	**0.0017**	**0.06**	**0.00**	**0.28**	**1.31**	**0.05**	**0.04**
	Tunnel Blank(30min)	*0.0029*	*0.00*	*0.00*	*0.00*	*3.29*	*0.00*	*0.00*
	CBD X 3	0.0199	13.64	0.20	14.18	1988.63	13.21	2.22
	CBD X 3	0.0215	14.61	0.15	13.57	1985.36	14.17	2.00
	Mean	**0.0207**	**14.13**	**0.18**	**13.88**	**1987.00**	**13.69**	**2.11**
	Stand. Dev.	**0.0011**	**0.69**	**0.04**	**0.43**	**2.31**	**0.68**	**0.16**
	Tunnel Blank(30min)	*0.0134*	*0.00*	*0.01*	*0.01*	*15.06*	*0.00*	*0.00*
DDC CNG-3 w/OxiCat	SS@55(30min)	0.0104	0.28	0.00	7.02	1048.82	0.28	0.50
	SS@55(30min)	0.0106	0.62	0.01	7.24	1041.68	0.62	0.37
	Mean	**0.0105**	**0.45**	**0.01**	**7.13**	**1045.25**	**0.45**	**0.44**
	Stand. Dev.	**0.0001**	**0.24**	**0.01**	**0.16**	**5.05**	**0.24**	**0.09**
	Tunnel Blank(30min)	*0.0028*	*0.00*	*0.00*	*0.00*	*1.63*	*0.00*	*0.18*
	CBD X 3	0.0194	6.21	4.03	12.70	2161.56	5.94	0.88
	CBD X 3	0.0211	6.09	4.14	13.92	2159.47	5.87	0.92
	Mean	**0.0203**	**6.15**	**4.09**	**13.31**	**2160.52**	**5.90**	**0.90**
	Stand. Dev.	**0.0012**	**0.09**	**0.08**	**0.86**	**1.48**	**0.05**	**0.03**
	Tunnel Blank(30min)	*0.0131*	*0.00*	*0.00*	*0.01*	*7.45*	*0.00*	*0.81*
DDC CNG-3	SS@55(30min)	0.0114	3.42	3.51	8.28	1034.51	2.89	0.98
	SS@55(30min)	0.0150	3.22	3.47	9.10	1038.42	2.88	1.25
	Mean	**0.0132**	**3.32**	**3.49**	**8.69**	**1036.47**	**2.89**	**1.12**
	Stand. Dev.	**0.0025**	**0.14**	**0.03**	**0.58**	**2.76**	**0.01**	**0.19**
	Tunnel Blank(30min)	*0.0033*	*0.00*	*0.00*	*0.00*	*0.49*	*0.00*	*0.00*
	CBD X 3	0.0293	8.68	8.15	16.27	2157.49	7.68	2.42
	CBD X 3	0.0267	8.63	7.92	14.82	2162.35	7.65	4.23
	Mean	**0.0280**	**8.66**	**8.04**	**15.55**	**2159.92**	**7.67**	**3.33**
	Stand. Dev.	**0.0018**	**0.04**	**0.16**	**1.03**	**3.44**	**0.02**	**1.28**
	Tunnel Blank(30min)	*0.0152*	*0.00*	*0.00*	*0.00*	*2.24*	*0.00*	*0.00*
Average Tunnel Blank - SS@55		0.0030	0.00	0.00	0.00	1.80	0.00	0.06
Stand. Dev.		0.0003	0.00	0.00	0.00	1.41	0.00	0.10
Average Tunnel Blank - CBD		0.0139	0.00	0.00	0.01	8.25	0.00	0.27
Stand. Dev.		0.0012	0.00	0.01	0.01	6.45	0.00	0.47

APPENDIX B

Table A. Emission of Specific VOCs by driving cycle (mg/mile ± 1 std. dev. of replicate measurements).

	Steady State Driving Cycle			Central Business District Driving Cycle		
	CWstprt	**DDC CNG-3 w/OxiCat**	**DDC CNG-3**	**CWstprt**	**DDC CNG-3 w/OxiCat**	**DDC CNG-3**
1,3 Butadiene	n.d.	n.d.	0.10 ± 0.02	n.d.	n.d.	0.39 ± 0.04
Benzene	n.d.	0.21 ± 0.15	1.47 ± 0.45	1.29 ± 1.21	0.60 ± 0.58	2.24 ± 0.28
Toluene	n.d.	0.71 ± 0.50	1.23 ± 0.40	0.35 ± 0.13	1.86 ± 0.32	1.15 ± 0.06
Ethylbenzene	n.d.	0.13 ± 0.09	0.20 ± 0.06	n.d.	0.31 ± 0.07	0.14 ± 0.10
m&p-Xylenes	n.d.	0.23 ± 0.16	0.31 ± 0.20	0.09 ± 0.08	1.06 ± 0.42	1.27 ± 0.90
Styrene	n.d.	n.d.	0.09 ± 0.09	n.d.	n.d.	n.d.
o-Xylene	n.d.	0.09 ± 0.06	0.13 ± 0.09	0.02 ± 0.04	0.44 ± 0.10	0.10 ± 0.07
Formaldehyde	24.6 ± 1.1	7.8 ± 2.9	357 ± 12	56.8 ± 0.5	38.4 ± 0.02	860 ± 60
Acetaldehyde	6.20 ± 0.49	4.8 ± 2.2	12.7 ± 0.49	19.4 ± 4.8	32.6 ± 2.7	50.7 ± 1.2
Acrolein	n.d.	n.d.	1.72 ± 0.80	n.d.	n.d.	3.91 ± 0.01
Acetone	1.40 ± 0.09	0.43 ± 0.09	n.d.	2.21 ± 0.83	4.67 ± 2.62	5.51 ± 2.94
Propionaldehyde	0.11 ± 0.06	n.d.	0.32 ± 0.03	n.d.	n.d.	3.62 ± 0.17
Butyraldehyde	0.16 ± 0.08	0.60 ± 0.42	0.11 ± 0.13	1.67 ± 0.49	1.89 ± 0.10	1.66 ± 0.66
Methyl Ethyl Ketone	n.d.	n.d.	0.43 ± 0.01	n.d.	n.d.	n.d.
Methacrolein	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	1.66 ± 0.42
Crotonaldehyde	n.d.	n.d.	0.67 ± 0.21	n.d.	n.d.	n.d.
Valeraldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	2.00 ± 0.06
m-Tolualdehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Hexanal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ethane	48.9 ± 1.0	1.57 ± 0.94	63.7 ± 0.62	155 ± 9	72.2 ± 3.5	217 ± 1
Ethene	4.01 ± 0.83	0.04 ± 0.03	159 ± 5	13.8 ± 2.2	3.27 ± 0.37	342 ± 1
Propane	1.78 ± 0.75	0.01 ± 0.01	6.51 ± 0.10	8.29 ± 0.29	4.98 ± 0.31	31.2 ± 1.1
Propene	0.19 ± 0.02	n.d.	12.6 ± 0.84	1.33 ± 0.58	0.40 ± 0.44	29.1 ± 0.01
Methylpropane	0.30 ± 0.07	0.02 ± 0.01	0.54 ± 0.10	0.87 ± 0.78	0.50 ± 0.01	4.15 ± 0.04
Ethyne	n.d.	n.d.	6.60 ± 0.32	n.d.	n.d.	16.6 ± 0.4
n-Butane	0.38 ± 0.06	0.03 ± 0.02	0.66 ± 0.02	1.35 ± 0.29	0.50 ± 0.12	4.18 ± 0.25
1-Butene	n.d.	n.d.	0.77 ± 0.16	n.d.	n.d.	1.86 ± 0.14
2-Methylpropene	n.d.	0.14 ± 0.01	0.20 ± 0.05	n.d.	n.d.	0.80 ± 0.11
2-Methylbutane	n.d.	0.02 ± 0.02	0.54 ± 0.04	0.14 ± 0.24	0.18 ± 0.07	2.08 ± 0.10
1-Pentane	n.d.	n.d.	0.13 ± 0.01	n.d.	n.d.	0.74 ± 0.05
1-Pentene	n.d.	n.d.	0.16 ± 0.04	n.d.	1.66 ± 0.66	n.d.
Total Carbonyl	32.5 ± 1.6	13.3 ± 4.8	373 ± 14	80.08 ± 0.1	77.6 ± 0.1	929 ± 61
Est. Total NMHC[a]	51 ± 9	9.2 ± 3.2	266 ± 31	184 ± 9	66[b] ± 24	588 ± 91

[a] Estimated as sum of quantifiable peaks measured from MR chromatogram – excludes carbonyls. [b]Est. Total NMHC is lower than sum of the peaks measured from the LE analysis due to an underestimation of C2 hydrocarbon emissions by the MR analysis. n.d. = not detected.

Table B. Tunnel blank 'emissions' following testing of a particular vehicle configuration (mg/mile equivalent).

	Steady State Cycle Equivalent[a]			Central Business District Cycle Equivalent[b]		
	CWstprt	**DDC CNG-3 w/OxiCat**	**DDC CNG-3**	**CWstprt**	**DDC CNG-3 w/OxiCat**	**DDC CNG-3**
1,3 Butadiene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzene	n.d.	0.10	0.01	n.d.	0.44	0.05
Toluene	n.d.	0.75	0.14	n.d.	3.26	0.59
Ethylbenzene	n.d.	0.45	0.02	n.d.	1.96	0.09
m&p-Xylenes	n.d.	1.06	0.05	n.d.	4.60	0.20
Styrene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
o-Xylene	n.d.	0.57	0.05	n.d.	2.48	0.22
Formaldehyde	3.07	3.33	4.58	13.4	14.5	19.9
Acetaldehyde	7.30	8.44	10.1	31.8	36.7	43.9
Acrolein	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetone	1.76	1.70	1.73	7.67	7.4	7.51
Propionaldehyde	n.d.	n.d.	0.63	n.d.	n.d.	2.74
Butyraldehyde	0.31	0.312	0.25	1.33	1.36	1.10
Methyl Ethyl Ketone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methacrolein	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Crotonaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Valeraldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
m-Tolualdehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Hexanal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ethane	0.05	0.07	0.12	0.22	0.31	0.54
Ethene	n.d.	0.01	0.16	n.d.	0.03	0.71
Propane	n.d.	0.22	0.28	n.d.	0.10	0.12
Propene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methylpropane	n.d.	0.01	0.32	n.d.	0.05	0.14
Ethyne	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
n-Butane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1-Butene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2-Methylpropene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2-Methylbutane	n.d.	n.d.	0.05	n.d.	n.d.	0.19
1-Pentane	n.d.	n.d.	0.01	n.d.	n.d.	0.03
1-Pentene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total Carbonyl	12.4	13.8	17.3	54.1	60.0	75.2
Est. Total NMHC[a]	n.d.	10.1	1.15	n.d.	43.7	5.01

[a] Mass emitted during tunnel blank test divided by 2.0 miles. [b] Mass emitted during tunnel blank test divided by 8.7 miles.

APPENDIX C

Motor Vehicle CNG Specifications

Specifications		***Value***
Hydrocarbons (expressed as mole percent)	Methane	88.0% (min.)
	Ethane	6.0% (max.)
	C3 and higher HC	3.0% (max.)
	C6 and higher HC	0.2% (max.)
Other Species (expressed as mole percent unless otherwise indicated)	Hydrogen	0.1% (max.)
	Carbon Monoxide	0.1% (max.)
	Oxygen	1.0% (max.)
	Inert Gases (Sum of CO_2 and N2)	1.5-4.5% (range)
	Sulfur	16 ppmv (max.)
	Water	a
	Particulate Mater	b
	Odorant	c

[a]The dewpoint at vehicle fuel storage container pressure shall be at least 10°F below the 99.0% winter design temperature listed in Chapter 24, Table 1, Climatic Conditions for the United States, in the American Society of Heating, Refrigerating and Air Conditioning Engineers (ASHRAE) Handbook, 1989 fundamentals volume. Testing for water vapor shall be in accordance with ASTM D 1142-90, utilizing the Bureau of Mines apparatus.

[b]The compressed natural gas shall not contain dust, sand, dirt, gums, oils, or other substances in an amount sufficient to be injurious to the fueling station equipment or the vehicle being fueled.

[c]The natural gas at ambient conditions must have a distinctive odor potent enough for its presence to be detected down to a concentration in air or not over 1/5 (one-fifth) of the lower limit of flammability.